

Lifshitz transitions and zero point lattice fluctuations in sulfur hydride showing near room temperature superconductivity

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Emerets's experiments on pressurized sulfur hydride have shown that H₃S metal has the highest known superconducting critical temperature $T_c = 203$ K. The Emerets data show pressure induced changes of the isotope coefficient between 0.25 and 0.5, in disagreement with Eliashberg theory which predicts a nearly constant isotope coefficient. We assign the pressure dependent isotope coefficient to Lifshitz transitions induced by pressure and zero point lattice fluctuations. It is known that pressure could induce changes of the topology of the Fermi surface, called Lifshitz transitions, but were neglected in previous papers on the H₃S superconductivity issue. Here we propose that H₃S is a multi-gap superconductor with a first condensate in the BCS regime (in the large Fermi surface with high Fermi energy) which coexists with a second condensates in the BCS-BEC crossover regime (located on a small Fermi surface spots with small Fermi energy) near the Γ and M point. We discuss the need of Bianconi-Perali-Valletta (BPV) superconductivity theory for superconductivity in H₃S. It includes both the correction of the chemical potential due to pairing and the configuration interaction between different condensates, neglected by the Eliashberg theory. Here the shape resonance in superconducting gaps, similar to Feshbach resonance in ultracold gases, gives a relevant contribution to amplify the critical temperature. Therefore this work provides some key tools needed in the search for new room temperature superconductors.

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I. INTRODUCTION.

Following early claims of 190 K superconductivity in sulfur hydride at very high pressure [1], new results of near room temperature superconductivity with $T_c = 203$ K i.e., at only -70 °C [2] have been presented on June 17, 2015 at Superstripes 2015 conference in Ischia, Italy [3] and they have triggered a very high scientific interest [4]. The recent work of Emerets's group [2] shows the Meissner effect and the pressure dependent critical temperature of H₃S and D₃S. These results have triggered today the materials research for room temperature superconductors in different hydrides at extreme high pressures [5–9].

The experimental discovery of near room temperature superconductivity in sulfur hydride H₂S at very high pressure was predicted by [10] to occur in the high pressure metallic H₃S phase, with $Im\bar{3}m$ lattice symmetry. Disproportion from $2(\text{H}_2\text{S}) + \text{H}_2$ to $2(\text{H}_3\text{S})$ occurs at very high pressure. The theoretical prediction of Duan et al. [10] has been obtained by using the successful theoretical approach used to predict crystalline structures at high pressure in material science: the evolutionary algorithm Universal Structure Predictor: Evolutionary Xtallography (USPEX) [11].

Many of preceding theoretical studies on this issue conclude that the superconducting phase in pressurized H₃S is described by the Eliashberg theory [10, 12–19] while Hirsh proposes the hole superconductivity model [20].

The Emerets's group research was motivated by the search for room temperature superconductivity predicted

to emerge in metallic hydrogen and hydrides [21–29].

The BCS theory [30] has given a microscopic description of the superconducting condensate many body wavefunction made of interacting Cooper pairs in a weak coupling regime, where the pairing is mediated by the conventional attractive phonon-exchange mechanism. We call here standard BCS theory the BCS formulas [30] obtained with many approximations, valid for a simple homogeneous crystal, with a single band and isotropic pairing, using a single value of the density of states at the Fermi level N_0 and a constant coupling constant λ . Moreover the standard BCS theory assumes a very small energy of the phonon and a very high electron density i.e., a high Fermi energy $\omega_0/E_F \ll 1$ called Migdal approximation [31] within the adiabatic Born-Oppenheimer approximation, where the electronic and ionic degrees of freedom can be rigorously separated. The prediction of the superconducting critical temperature in the frame of the standard BCS theory approximations has required the introduction of the electron-electron repulsive interaction and corrections due to strong coupling given by the McMillan [32, 33] and the Eliashberg [34] formula.

It was rapidly well accepted that the critical temperature cannot be larger than 30 K in the frame of standard BCS theory based only on the role of high energy phonons and strong electron-phonon coupling [22, 24, 28]. In fact in the single band approximation T_c increases with both phonon energy and coupling strength but for extreme strong electron-phonon coupling the electron liquid at low temperature prefers to order in the real space, forming electronic crystals like, charge density waves, spin

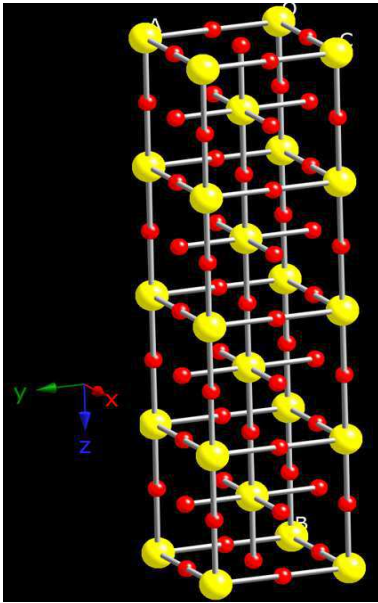


FIG. 1: (Color online) The crystalline structure of H_3S with $Im\bar{3}m$ lattice symmetry, with two formula units per unit cell, with sulfur (yellow large spheres) and hydrogen atoms (red small spheres). The linear S-H-S hydrogen bonds along the a,b and c axis in the $Im\bar{3}m$ lattice of H_3S , form a first 3D network of three linear chains of covalent bonds crossing at the sulfur atom at $S1(0,0,0)$, which coexists with a second 3D network of other three linear chains of covalent bonds (solid black lines) crossing at the sulfur atom at $S1(0.5,0.5,0.5)$.

density waves, which compete with the superconducting phase. Moreover if superconductivity survives increasing electron-phonon coupling, the critical temperature decreases since the phonon energy is pushed toward zero. In these regime the lattice structure collapses and the system is in the verge of a catastrophe. Therefore it was known that materials research for room temperate superconductivity cannot be driven simply by looking to increase the phonon energy and coupling strength in the cooper pairing. The theoretical predictions of high T_c in solid hydrogen and hydrates at high pressure were based not only on the high frequency phonons mediating the pairing in solid hydrogen or hydrates but also on joint control of the electron electron interaction via the changes of the dielectric constant controlling the repulsive electron-electron interaction and the Coulomb energy [21–29] which can become negative [22, 24, 28] for an electronic system in the low density limit.

The self consistent quantum many body theory of superconductivity, avoiding the BCS approximations, was made by Bogoliubov [35], giving the fundamental spectrum of excited quasiparticles. It was developed by Gorkov [36] and Blatt [37] including the contribution to the critical temperature of the condensation energy, related with Josephson-like [40] terms, [38, 39] and considering multiple symmetries of possible multiple condensates with a single critical temperature [41]. A second

route to rise the critical temperature of superconductivity toward the maximum possible energy, $K_B T_c / E_F \sim 1$ was proposed in 1994 based on the non standard BCS theories where the control of T_c can be achieved not only by increasing the pairing strength but also by the control of the condensation energy, via a pair exchange mechanism between condensates, called the shape resonance in superconducting gaps [42–45]. It was proposed that cuprates are actually complex inhomogeneous materials with lattice quenched disorder, lattice modulations and short range charge density waves giving multiple Fermi surface arcs where in each Fermi arc there is a different superconducting condensate. One of these condensates is in the polaronic regime, where the Migdal approximation is violated $\omega_0 / E_F \sim 1$, and the condensate is in the BCS-BEC crossover regime while the other condensates are within the Migdal approximation $\omega_0 / E_F \ll 1$. In 1996-1998 [46–50] a superconductivity theory was developed by Bianconi, Perali, Valletta (BPV) based on the Blatt [37] and Legget [41] theories. The superconducting critical temperature here is not only controlled only by the cooper pair formation but also by the exchange terms between pairs. These terms control the condensation energy and phase coherence and are unavoidable ingredients for the formation and stability of high temperature superconducting condensate with short coherence length. A similar mechanism, called Feshbach resonance, was proposed later to increase the critical temperature for the formation of the superfluid condensate in ultra-cold atoms [51, 52]. Later other many body theories have been proposed aimed to control the condensation energy and the global phase coherence in superconductors and superfluids [53, 54].

Details of the normal metallic phase become key ingredients in these non standard BCS theories: a) the complex Fermiology, beyond the single band model; b) the formation of charge density waves and polaronic Wigner crystals involving the electronic component in n-th Fermi surfaces beyond the Migdal approximation $\omega_0 / E_{nF} \sim 1$; c) the strong electronic correlations in the electron fluid with very low Fermi energy, beyond the usually assumed Fermi gas approximation; e) the anomalous or negative dielectric response controlling the electron-electron interaction; f) the complex inhomogeneous spatial geometry in systems with nanoscale phase separation [55] induced by electron-lattice interaction and lattice misfit strain [56] which can give also insulator to superconductor phase transitions [57].

II. SUPERCONDUCTIVITY IN BINARY INTERMETALLICS: A15 AND DIBORIDES

The overall features of superconductivity in H_3S show that it is like other binary intermetallics, as diborides and A15 systems therefore we shown in figure 2 the evolution of the maximum critical temperature of diatomic intermetallics.

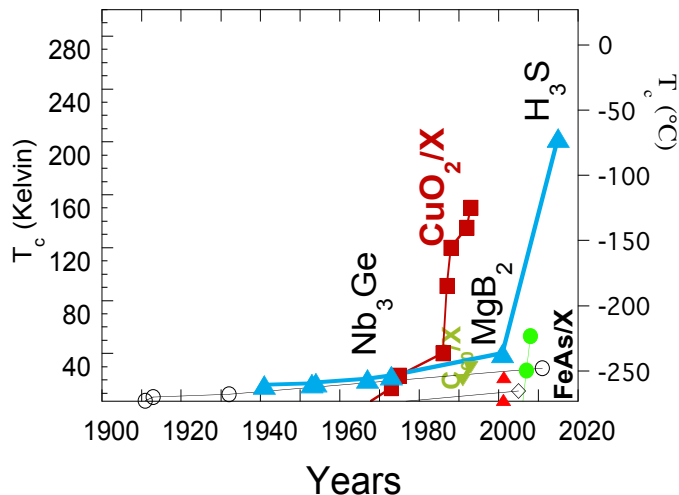


FIG. 2: (Color online) The superconducting critical temperature of superconducting elements, open black circles, binary intermetallics, filled blue triangles, and ternary and quaternary oxide layered perovskites made of CuO_2 -atomic layers with different X spacer layers (filled red squares) coefficient as a function of the year of the discovery.

A15 compounds (like Nb_3Ge) have the same $Im\bar{3}m$ lattice structure [58] as H_3S above 100 GPa (shown in Fig.1) which is made of two intertwined networks of atomic wires running in 3D as noticed by Friedel [59, 60] within a 3D density of states [61–63] and superconductivity appears in highly inhomogeneous phases at the edge of a lattice catastrophe due to incipient structural phase transitions [64–66] giving complex pattern of defects and local lattice fluctuations [67–69].

Following the discovery of superconductivity in MgB_2 in 2001 it was first proposed [70] the breakdown of the Eliashberg theory and the need of BPV theory including shape resonance to describe this system made of multiple condensates and a single critical temperature. The breakdown of the Eliashberg theory was rapidly accepted by the community. The theoretical assumptions used by standard BCS theory, considering a single band and single gap, fail due to anisotropic pairing in the clean limit. The standard BCS formulas failed to predict accurately the unusually high transition temperature, the effects of isotope substitution on the critical transition temperature, and the anomalous specific heat of MgB_2 . While some authors proposed the multi-band superconductivity theory [71] in the clean limit and weak coupling, it was rapidly shown the need of strong coupling anisotropic two band Eliashberg theory to describe this unexpected novel superconducting phase [72, 73]. The isostructural AlB_2 system with only π electrons at the Fermi level becomes superconductor only when the chemical doping pushes the top of the σ band above the chemical poten-

tial giving a Lifshitz transition for the appearing of two small hole-like σ Fermi pockets [74]. Moreover because of zero point atomic fluctuations [75, 76], the Fermi energy in the σ bands is time and space dependent therefore the Migdal approximation $\omega_0/E_F < 1$, is violated and the Eliashberg theory fails, when the Fermi energy is tuned over a large energy range of 600 meV above the bottom of band edge [77, 78]. Therefore in spite of the conventional phonon mediated pairing, the 40 K superconducting phase in magnesium diboride needs a non standard BCS theory. Considering all data collected in diborides doped with Sc and Al for Mg or with C for B it was possible to give a theoretical interpretation of the variation of the two superconducting gaps and the critical temperature as a function of the energy separation between the top of the σ band and the chemical potential using the BPV theory [79]. The superconducting σ gaps are much larger than the gaps in the large π Fermi surfaces and evolve as a function of the energy separation of the top of the σ band and the chemical potential [79]. The small percentage of the partial electronic density of states, $\text{DOS}(\sigma)$, relative to the total $\text{DOS}(\text{tot})$, usually entering in the standard McMillan formula for T_c , gives a large superconducting σ gap, which drives the full system to the highest critical temperature known in binary intermetallics, before the recent discovery of Eremets's group [2]. In a single band metal, where $\omega_0/E_F \sim 1$ the Migdal and the adiabatic approximations [76] fail, the system enters in the BCS-BEC crossover [80, 81] and both weak coupling BCS [30] and strong coupling Eliashberg theories breakdown. On the contrary the superconductivity phase in a system with multiple condensates, where only one or two of the Fermi surface spots are in the BCS-BEC crossover while other condensates in the large Fermi surfaces are in the BCS regime, can be described by the theory of Bianconi Perali Valletta (BPV) [41, 79] correctly describing the multi-gap superconductivity at the BCS-BEC crossover avoiding standard approximations. The condensation energy of the pairs is determined by many body configuration interaction between pairs forming the single macroscopic superconducting quantum coherent phase. The condensation energy [38] is relevant a) in the BCS-BEC crossover $\Delta_n/E_{Fn} \sim 1$ and in the formation of the superconducting quantum coherent phase with a single T_c in a system made of multiple gaps Δ_n in different bands with different Fermi energies E_{Fn} . The shift of the chemical potential going from the normal to the superconducting phase below T_c , becomes a key term in MBBC, while on the contrary it is considered to be negligible in standard BCS. The results of the BPV theory applied to doped magnesium diboride [79] show that it is in a regime of multiple condensates with different symmetry with the key role of the shape resonance in the superconducting gaps between one condensate in the BCS-BEC crossover, in the σ band, and other condensates in the BCS regime, in the π bands, with an essential Josephson-like pair exchange term.

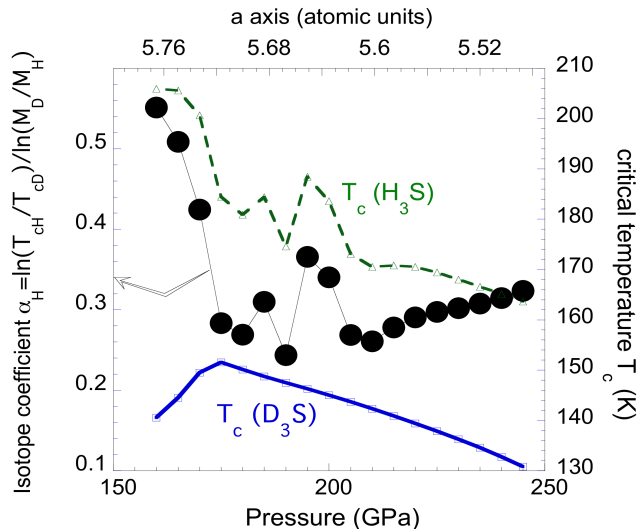


FIG. 3: (Color online) The pressure dependent isotope coefficient as a function of pressure (filled circles) calculated by interpolation of the experimental data of the critical temperature of H_3S (dashed green line) and D_3S solid blue line reported by Droz et al. [2]

III. LIFSHITZ TRANSITIONS.

The topological changes of the Fermi surface of the normal phase caused by the lattice strain (as a response to pressure), misfit strain, chemical substitution, variation of the electronic density) are called Lifshitz transitions [82]. In many cases Lifshitz transitions appear on points or lines of high symmetry in the Brillouin zone and are associated with changes of the symmetry or dimensionality of the wave functions of the electrons at the Fermi level in critical Fermi surfaces. The Lifshitz transitions are revealed experimentally by anomalies in lattice parameters, in the density of states near the Fermi energy, in elastic properties, in anomalous thermodynamic and transport properties of metallic materials [83]. Lifshitz [82]. noted that at zero temperature, $T = 0$, Lifshitz transitions are true phase transitions of order 2.5 (as in Ehrenfest's classification) therefore are called "2.5 Lifshitz transition". A sharp Lifshitz transition at $T=0$, at high temperature shows a crossover character. In presence of strong interactions the 2.5 phase transition becomes first order with a phase separation between two phases where the chemical potential in each phase is shifted above and below the Lifshitz transition respectively [78, 84, 85] driving the system well tuned at a Lifshitz transition on the verge of a lattice catastrophe as shown in the case of Al_5 and diborides. While in the early times the interest was focused on Lifshitz transitions in single band metals, now the interest is addressed to Lifshitz transitions in multi-band metals with different Fermi surfaces showing multi-gap

superconductivity. The shape resonance mechanism considers the relevant contribution, near the Lifshitz transition, of the exchange interaction between pairs in the hot spots and in all other points of the Fermi surfaces in the k space. We have learned that the "Devil is in the details", in fact for the optimization of a high critical temperature it is necessary to reach particular Lifshitz transitions where a small number of electrons in a new appearing Fermi surface (the hot spot) are in the extreme strong coupling regime in the antiadiabatic $\omega_0/E_{Fn} \sim 1$ regime in the normal phase without the lattice catastrophe since the majority of the electron gas is in large Fermi surfaces well in the Migdal approximation $\omega_0/E_{Fn} < 1$. The shape resonance in superconducting gaps is a Josephson-like term describing a contact interaction between pairs which increases the critical temperature for the pairs condensation, very similar to the Feshbach resonance in ultracold gases [51, 52] driving up the ratio between $k_B T_c$ and the Fermi energy up to value of 0.2. In the superfluid phase in the hot spot is in the BCS-BEC crossover $\Delta_n/E_{Fn} \sim 1$ [86] and the shape resonances in the superconducting gaps can be optimized to amplify the critical temperature to the highest value [50]. A large zero point lattice motion is a key term in the theory of the shape resonance in superconducting gaps which is in action in the proximity of the Lifshitz transitions. It was proposed to play a key role in cuprates [42, 46, 49, 87–89], it was verified to be in action in diborides [74, 79] and it was confirmed in iron based superconductors [90–99]. We discuss below the failure of the standard Migdal approximation and of the breakdown of Eliashberg theory in H_3S . The large electron-phonon coupling and the high frequencies of H-phonons contribute to rise T_c [10, 15, 19] but we claim the need of theories beyond Eliashberg theory. like the multigap BCS-BEC crossover (MBBC) theory and the BPV shape resonance mechanism to describe the gaps in the new small Fermi surfaces appearing at the Lifshitz transitions controlled by pressure and their configuration interaction with the gap in the large Fermi surface.

IV. ISOTOPE EFFECT IN H_3S .

The isotope effect in H_3S [1] has provided a direct evidence of the involvement of the lattice degree of freedom in the pairing process. Therefore the isotope effect in sulfur hydrate at high pressure H_3S has been interpreted as ruling out theories of unconventional superconductivity (based only on spin liquid models or magnetic interactions) and supporting conventional theories of superconductivity based on the role of lattice fluctuations. However the standard BCS theory predicts a pressure independent isotope coefficient 0.5 while in non standard BCS theories, like in the multigap anisotropic BCS, the isotope coefficient deviates from 0.5 as in magnesium diboride where it is 0.26 [100]. From the new results reported by Droz et al. [2] we have extracted the isotope coefficient as a function of pressure shown in figure 3.

We can see in figure 3 large variations of the isotope coefficient reaching a minimum of 0.2 and first maximum reaching 0.5 at 170 GPa and a second peak at 240 GPa. The anomalous pressure dependent isotope coefficient has been found in cuprates superconductors as a function of doping [49, 88, 89] with anomalies where the chemical potential crosses Lifshitz transitions driven by pressure. Therefore the data in figure 3 indicate the possible presence of Lifshitz transitions in the pressure range showing near room temperature superconductivity.

V. BAND STRUCTURE CALCULATION OF H_3S AS A FUNCTION OF PRESSURE

We have performed preliminary band structure calculations [101] of H_3S with $Im\bar{3}m$ lattice symmetry made using the linear muffin-tin orbital (LMTO) method [102, 103] and the local spin-density approximation (LSDA) [104]. We show in Fig. 4 the dispersion of the bands crossing the chemical potential in the $\Gamma - M$ direction.

Self-consistent paramagnetic calculations are made for a simple cubic unit cell containing 8 sites totally, used for A15 compounds with the same crystalline structure. The details of the method have been published earlier [105–108]. The present calculations are in good agreement with previous band structure calculations [15–19]. We confirm the presence of a narrow peak of the occupied total Density of States (DOS) very close to the chemical potential at 200 GPa i.e., for $a=5.6$ a.u. The narrow peak in the total DOS in a narrow energy range around the chemical potential is shown in Fig. 5. While previous papers have stated that this peak is pinned at the zero energy, we show in Fig. 5 that the energy position of this peak relative to the chemical potential shifts with pressure. The narrow peak of the DOS is pushed toward high energy by pressure and it crosses the chemical potential at the highest P for the lattice constant smaller than $a=5.8$ a.u..

The narrow peak of the DOS peak is related with the flat dispersion of bands in the $\Gamma - M$ direction in the energy range of 2 eV below the chemical potential. shown in Fig. 4. The band structure shows a first steep band with very large energy dispersion with its band edges at about 20 eV away from the chemical potential. This first band gives the large Fermi surface shown in [13]. There are three other small Fermi surface pockets centered around the Γ point shown in Fig. 4 for different lattice parameter a .

The tops of the hole-like bands near the Γ point are below E_F at low pressure P but they move above the chemical potential above 130 GPa pressure as shown in Fig. 4. The edges of these bands cross the chemical potential as function of P giving topological Lifshitz transitions with the appearing of new Fermi surfaces. Moreover there is a small Fermi surface hole pocket due to the crossing of one band at about 2/3 of the $\Gamma - M$ distance indicated

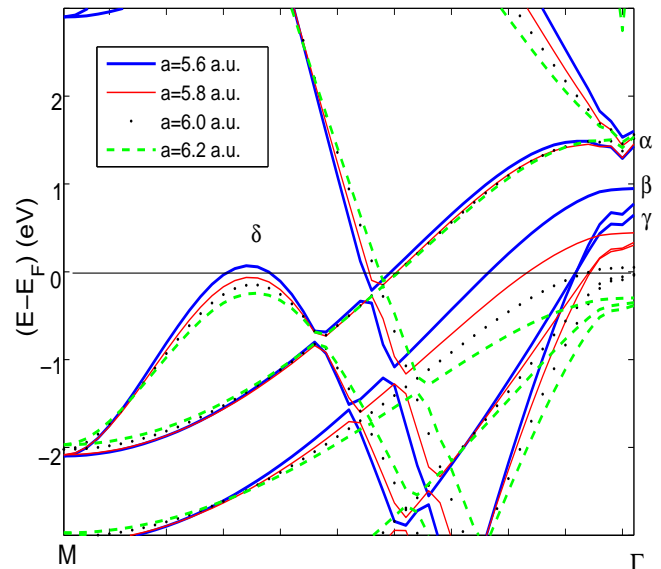


FIG. 4: (Color online) The dispersion of the bands in the electronic structure of H_3S calculated using the simple cubic cell, used for A15 compounds with $Im\bar{3}m$ structure, between M and Γ points. The band dispersion in this direction gives the narrow DOS peak near the Fermi energy. Moreover we show the variation of this bands at different pressure with changing the lattice parameter between $a=6.2$ a.u and $a=5.6$. We show that there are bands (β and γ) forming 3 small Fermi surfaces at the Γ point and another band crosses the zero energy at the point indicated by δ which gives a new small hole pocket at high pressure.

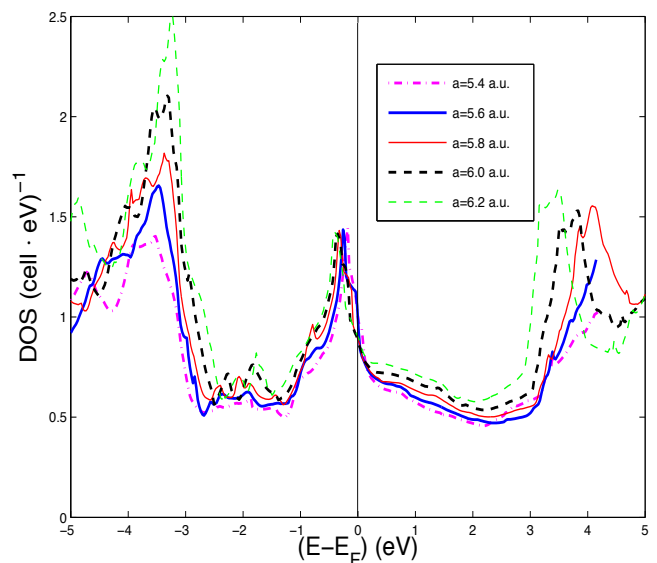


FIG. 5: (Color online) The total DOS for H_3S at different lattice constants. A sharp peak of the DOS crosses the chemical potential at high pressure.

by δ in Fig. 4 which appears only for lattice parameters smaller than $a \sim 5.8$ a.u., i.e. in the pressure range of highest P when T_c is highest. The top of this band goes from -0.2 eV below the chemical potential to $+0.1$ eV when a decreases from 6.2 to 5.6 a.u.. Finally we associate the crossing of the chemical potential by this band at δ in Fig. 4 with the Fermi level crossing of the narrow DOS peak in Fig. 5.

Let us now consider the fact that because of the zero-point motion (ZPM) the different Fermi energies in the small pockets show large energy fluctuations like in magnesium diboride. The ZPM is large because of the small mass of H atoms and it has large effects on the fluctuations of electronic structure. Such effects have been shown to be important in several different materials, even if their atomic masses are larger [112–114]. Lattice fluctuations can perturb spin waves and phonons in high- T_c cuprates and it cannot be neglected if superconductivity relies on few phonons coupled with particular bands [115]. The Debye temperature for H phonons is high ($\sim 1800K$) and the amplitude of lattice fluctuations from ZPM is large already at low T . With a force constant $K = M\omega^2$ of 7 eV/\AA^2 we obtain an average amplitude u of the order 0.15 \AA . As seen in Fig. 5, the first high lying valence band has a width is about 2 Ry. This makes the band dispersion and Fermi velocities high in the first band forming the Fermi surface centered at the R point. The effects of energy band broadening is negligible here since the chemical potential is far from band edges. The large effect of the zero point motion is on the small Fermi pockets near the Γ point. The low- T energy band fluctuations in materials with narrower band widths has been found to be about 20 meV for u in the range 0.03-0.04 \AA [112, 113, 115]. From an extrapolation of these values to the conditions in H_3S we estimate that the band energy fluctuation can be of the order of 160 meV for H-bands. Therefore when the chemical potential is tuned by pressure near a Lifshitz transition, so that the En_F in one of the bands is of the order of 160 meV the topology of the small Fermi surfaces made of small hole- or electron-pockets shows strong dynamical fluctuations controlled by the zero point lattice fluctuations.

Figure 6 shows the energy position of the top of the 3 bands at the Γ point and the band at about $2/3$ of the $\Gamma-M$ distance as a function of pressure. The energy spread due to zero point lattice fluctuations is indicated by the red area for states at the Γ point by the yellow area for the states at $\Gamma-M$ point. The shift of the energy position of the narrow peak in the DOS near the chemical potential tracks the top of the band at the $\Gamma-M$ point indicates that the chemical potential here is tuned at the Lifshitz transition appearing around 170 GPa for the appearing of this new Fermi surface. Finally these results show that in superconducting pressurized sulfur hydrate metal is made of one large Fermi surface and four small pockets tuned by pressure at Lifshitz transitions like doping tune the metal in cuprates at Lifshitz transitions for the appearing new Fermi surface arcs [42, 46, 49].

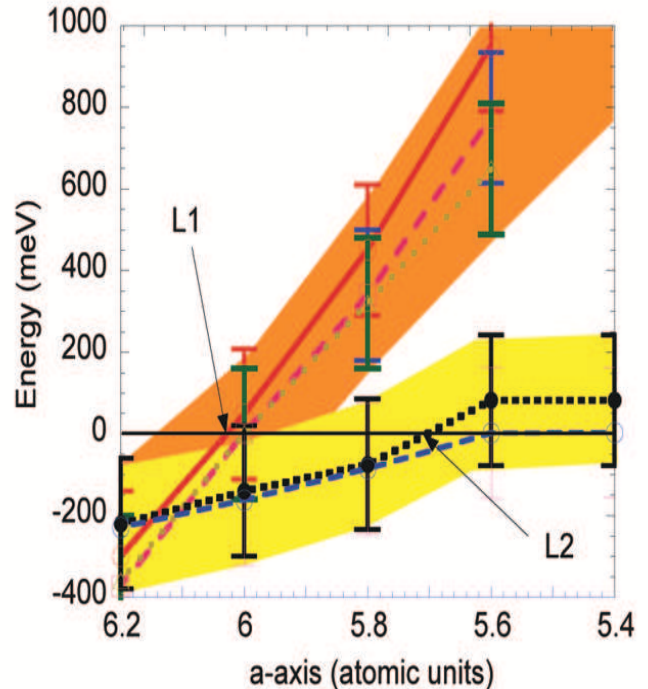


FIG. 6: (Color online) Energy shift of the tops of the three hole-like bands at the Γ point (solid red line, dashed red line and dotted yellow line) crossing the chemical potential at 100 GPa, where the errors bars and the red region indicates the zero point energy fluctuations of the band edges. The filled black dots and the dotted black line show the energy shift of the top of the band crossing the chemical potential at about $2/3$ of the $\Gamma-M$ distance of the Brillouin zone. The open circles and the blue dashed line show the energy shift of the narrow peak of DOS near the chemical potential

VI. BPV THEORY FOR MULTI-GAPS SUPERCONDUCTORS AT THE BCS-BEC CROSSOVER

The standard BCS theory in undergraduate courses considers a homogeneous single band metal and describes the cooper pairing in weak coupling limit as due to quantum exchange of a low energy phonon between two high energy electrons at the Fermi level in the Migdal approximation where the gap energy is much smaller than the Fermi energy and the gap to critical temperature ratio is equal to 1.75. Non standard BCS theories diverge substantially from the standard BCS theory. Let us simplify a long story by classify 7 different non standard BCS theories. Let us start with the first group considering a single effective band, in a dirty limit, giving a single condensate: 1A) the standard strong coupling Eliashberg theories considering a high energy phonon or vibron (a quantum of intramolecular vibration) interacting with electrons having a large Fermi energy $\omega_0/E_F \ll 1$. Most of previous theories for high T_c in sulfur hydrates

have proposed this approach for a large phonon frequency and strong coupling; 1B) the theories considering the case of a low density electron gas beyond the Migdal approximation $\omega_0/E_{Fn} > 1$ where the single condensate is formed by BEC condensation or by BCS-BEC crossover $\Delta_n/E_F \sim 1$; 1C) non standard BCS theories which consider pairing mediated by electronic excitations, called exciton theories.

The second group of non standard BCS theories considers the anisotropic BCS theory, in the clean limit, therefore they focus on multi-gap superconductivity where multiple gaps are formed in different spots of the k -space. These non standard BCS theories consider metals with multiple bands with different symmetry crossing the chemical potential: 2A) The multiband BCS model where all multiple Fermi surfaces are in the BCS limit; 2B) the Fermi-Bose model where the Fermi level of a first band is degenerate with a single level, occupied by paired electrons. Here a BCS condensate coexists with bosons which undergoes a Bose condensation; 2C) the extreme case of superconductivity driven mostly by exchange like interband pairing with very weak, or no intraband pairing; 2D) The theory of *shaperesonance* in superconducting gaps for multi-condensates with a small interband pairing, emerging in metals where: a first small charge density in small Fermi surfaces form condensates in the BEC-BCS crossover, beyond Migdal approximation, which coexists with a majority of charges in large Fermi surfaces forming BCS condensates.

A third group of theories consider the case of systems with relevant electronic and lattice inhomogeneity with insulator to superconductor transitions in presence of nanoscale phase separation where the Josephson-like interaction between localized condensates play a key role.

Here we focus on the BPV (Bianconi, Perali, Valletta) theory which correctly include the *shape resonance* (2D) mechanism, proposed for cuprates, [42, 46, 49, 50, 87–89] diborides [74, 79] and iron based superconductors [90–92]. This mechanism (2D) is proposed here for sulfur hydrides at very high pressure following the reported evidence for Lifshitz transitions driven by high pressure.

We recall below the BPV theory for multi gap superconductors at the BCS-BEC crossover including shape resonances. Let us consider a system made of multiple bands with index n , having a steep free electron like dispersion in the x direction and a flat band-like dispersion in the y direction. The energy separation between the chemical potential and the bottom of the n -th band defines the Fermi energy of the n -th band. This formulation was proposed for complex systems in presence of one-dimensional lattice modulation or one-dimensional charge density waves where the chemical potential is tuned near a Lifshitz transition like in magnesium diborides, A15, cuprates, iron based superconductors and we propose here for sulfur hydrate at high pressure.

The formula for the superconducting critical temperature T_c in a anisotropic multi-gap non standard BCS scheme is given by the linearized BCS equation consider-

ing the simplest case of a two dimensional system [49] but the extension to three dimensional system [79] is trivial.

$$\Delta_{n,k_y} = -\frac{1}{2N} \sum_{n',k'} V_{\mathbf{k},\mathbf{k}'}^{n,n'} \frac{\tanh(\frac{E_{n,k_y} + \epsilon_{k_x} - \mu}{2T_c})}{E_{n,k_y} + \epsilon_{k_x} - \mu} \Delta_{n',k'_y}, \quad (1)$$

where the energy dispersion is measured with respect to the chemical potential.

We consider a superconductor with multiple gaps Δ_{n,k_y} in multiple bands n with flat band-like dispersion in the y direction and steep free-electron-like dispersion in the x direction for a simple model of a two dimensional metal with a one-dimensional superlattice modulation in the y -direction. The self consistent equation for the gaps at ($T = 0$) where each gap depends on the other gaps is given by

$$\Delta_{n,k_y} = -\frac{1}{2N} \sum_{n',k'_y,k'_x} \frac{V_{\mathbf{k},\mathbf{k}'}^{n,n'} \Delta_{n',k'_y}}{\sqrt{(E_{n',k'_y} + \epsilon_{k'_x} - \mu)^2 + \Delta_{n',k'_y}^2}}, \quad (2)$$

where N is the total number of wave-vectors in the discrete summation, μ is the chemical potential, $V_{\mathbf{k},\mathbf{k}'}^{n,n'}$ is the effective pairing interaction

$$V_{\mathbf{k},\mathbf{k}'}^{n,n'} = \tilde{V}_{\mathbf{k},\mathbf{k}'}^{n,n'} \times \theta(\omega_0 - |E_{n,k_y} + \epsilon_{k_x} - \mu|) \theta(\omega_0 - |E_{n',k'_y} + \epsilon_{k'_x} - \mu|) \quad (3)$$

Here we take account of the interference effects between the wave functions of the pairing electrons in the different bands, where n and n' are the band indexes, $k_y(k'_y)$ is the superlattice wave-vector and $k_x(k'_x)$ is the component of the wave-vector in the free-electron-like direction of the initial (final) state in the pairing process.

$$\tilde{V}_{\mathbf{k},\mathbf{k}'}^{n,n'} = -\frac{\lambda_{n,n'}}{N_0} S \times \int_S \psi_{n',-k'_y}(y) \psi_{n,-k_y}(y) \psi_{n,k_y}(y) \psi_{n',k'_y}(y) dx dy, \quad (4)$$

Here N_0 is the DOS at E_F without the lattice modulation, $\lambda_{n,n'}$ is the dimensionless coupling parameter, $S = L_x L_y$ is the surface of the plane and $\psi_{n,k_y}(y)$ are the eigenfunctions in the 1D superlattice. The gap equation need to be solved iteratively. The anisotropic gaps dependent on the band index and on the superlattice wave-vector k_y . According with Leggett [41] the ground-state BCS wave function corresponds to an ensemble of overlapping Cooper pairs at weak coupling (BCS regime) and evolves to molecular (non-overlapping) pairs with bosonic character and this approach remains valid also if a particular band is in the BCS-BEC crossover and beyond Migdal approximation because all other bands are in the BCS regime and in the Migdal approximation.

However in this anomalous regime, where Eliashberg theory breakdown, on density: by increasing coupling or decreasing the density by approaching the band edge, the chemical potential μ results strongly renormalized with respect to the Fermi energy E_F of the non interacting system, and approaches minus half of the molecular binding energy of the corresponding two-body problem in the vacuum. In the case of a Lifshitz transition, described in this paper, all electrons in the new appearing Fermi surface condense forming a condensate in the BCS-BEC crossover. Therefore at any chosen value of the charge density for a number of the occupied bands N_b , the chemical potential in the superconducting phase should be renormalized by the gap opening at any chosen value of the charge density ρ using the following formula:

$$\begin{aligned} \rho &= \frac{1}{L_x L_y} \sum_n \sum_{k_x, k_y}^{N_b} \left[1 - \frac{E_{n, k_y} + \epsilon_{k_x} - \mu}{\sqrt{(E_{n, k_y} + \epsilon_{k_x} - \mu)^2 + \Delta_{n, k_y}^2}} \right] \\ &= \frac{\delta k_y}{\pi} \sum_{n=1}^{N_b} \sum_{k_y=0}^{\pi/l_p} \int_0^{\epsilon_{min}} d\epsilon \frac{2N(\epsilon)}{L_x} + \int_{\epsilon_{min}}^{\epsilon_{max}} d\epsilon \frac{N(\epsilon)}{L_x} \\ &\quad \times \left(1 - \frac{E_{n, k_y} + \epsilon_{k_x} - \mu}{\sqrt{(E_{n, k_y} + \epsilon_{k_x} - \mu)^2 + \Delta_{n, k_y}^2}} \right). \end{aligned} \quad (5)$$

taking the increment in k_y as $\delta k_y = 2\pi/L_y$ for a size of the considered surface $aL_x L_y$ and in the range

$$\begin{aligned} \epsilon_{min} &= \max [0, \mu - \omega_0 - E_{n, k_y}], \\ \epsilon_{max} &= \max [0, \mu + \omega_0 - E_{n, k_y}], \\ N(\epsilon) &= \frac{L_x}{2\pi \sqrt{\frac{\epsilon}{2m}}}, \end{aligned}$$

VII. CONCLUSION.

In this work we have presented the breakdown of the Eliashberg theory for H_3S , in fact the electronic structure of sulfur hydrides H_3S with $Im\bar{3}m$ lattice structure as function of pressure shows Lifshitz transitions revealed by band crossings at E_F and by the shift of the narrow peak in the density of states below the chemical potential pushed above it by lattice fluctuations associated with the hydrogen zero point motion. We have discussed the presence of two topological Lifshitz transitions at two critical pressures $P_{c1} = 110$ GPa, and $P_{c2} = 175$ GPa by pressure dependent electronic structure calculations of H_3S . At the first Lifshitz transition, around $P_{c1} = 110$ GPa, three new Fermi surface spots appear at the γ point pushed up by pressure. These anisotropic bands are characterized by a flat dispersion in the $\Gamma - M$ direction and a steep dispersion in the $\Gamma - R$ direction. The second Lifshitz transition at $P_{c2} = 180$ GPa is due a new where the experimental critical temperature is nearly constant.

The amplitude of the energy fluctuations of this band edge due to atomic zero point motion has been calculated and we have found that it pushes this DOS peak above the chemical potential. Therefore dynamical energy fluctuations of the band edge due to zero point motion of the hydrogen atoms is of high relevance. We find a colossal zero point energy fluctuation which induces a 160 meV energy fluctuation of the Lifshitz transitions. The present results show that the condensates in the 4 small hole pockets around the Γ point and the small Fermi surface in the $\Gamma - M$ direction are beyond the Migdal approximation $\omega_0/E_F \sim 1$, including lattice dynamical zero point fluctuations. In particular the condensate in the hole-like δ Fermi surface pocket, associated with the sharp quasi-1D peak in the DOS, pushed at the chemical potential by pressure, is clearly in the BCS-BEC crossover regime, coexisting with other condensates in the BCS regime in other large Fermi surfaces in the pressure range where the superconducting critical temperature is near room temperature.

The emerging scenario is pairing in sulfur hydrides at high pressure in a dynamical landscape where key energy parameters have all the same magnitude i.e, of the order of 160 meV: 1. the energy separation between the average position of the n^{th} band edge and the chemical potential, defined as the n^{th} Fermi energy controlling the "appearing or disappearing Fermi surface spot" Lifshitz transition in the Fermi surface topology, 2. the energy separation of a peak in the Density of States and the band edge, usually controlling the "Neck opening" Lifshitz transition 3. the amplitude of the energy fluctuation of the critical Fermi surfaces associated with zero point lattice fluctuations 4. The energy of the pairing interaction defining the energy of the cut-off for the formations of pairs away from the chemical potential

In this scenario the BCS approximations used in the standard BCS theory are no more valid and the critical temperature is controlled not only by the energy of the changed boson, w_0 , and the effective electron-phonon coupling (given by the product of the density of states times the electron-phonon coupling constant) but also by the condensation energy. While in the standard Eliashberg theory, the correction to the chemical potential induced by electron-phonon coupling is ignored on the verge of the Lifshitz transition this correction, which has much impact, is considered in the Multi-gaps BCS-BEC Crossover theory. In this situation the chemical shift from the normal to the condensed phase below T_c is no more negligible, and the coupling should be renormalized by a factor, given by the quantum overlap of the condensed pairs in cuprates [46, 49, 50, 87] diborides [72, 77, 79] and iron based superconductors [90–96].

Finally this paper shows the breakdown of Eliashberg theory for pressurized hydrides, supports the role of phonons [10, 15–19] but the presence of Lifshitz transitions tuned by pressure need the use of the Multi-gaps BCS-BEC Crossover theory including shape resonances.

Further work is needed to investigate i) the divergent

amplitude of lattice fluctuations near the $R3m$ to $Im\bar{3}m$ 2nd order structural transition around 180 GPa, ii) the large mass difference between H and S which requires the consideration of different amplitudes of u for the two types of atoms, and it should allow for E and k dependences for the energy fluctuations of Lifshitz transitions. The electronic band calculations should be extended to large supercells needed for more precise estimates of energy fluctuations of the electronic structure associated with spacial structural fluctuations. We think that the

discovery of superconductivity in sulfur hydrates very near room temperature has narrowed the number of possible road maps toward new functional superconducting materials. Further fundamental research on the mechanism of room temperature superconductivity in these new phase of matter are needed to clarify this emerging physical scenario and they will allow the definition of a protocol for the material design of new functional room temperature superconductors.

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